

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
13 May 2004 (13.05.2004)

PCT

(10) International Publication Number
WO 2004/039724 A1

- (51) International Patent Classification⁷: **C01B 33/26**
- (21) International Application Number:
PCT/EP2003/007579
- (22) International Filing Date: 14 July 2003 (14.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0209085 18 July 2002 (18.07.2002) FR
- (71) Applicant (for all designated States except US): **EAST-MAN KODAK COMPANY** [US/US]; 343 State Street, Rochester, NY 14650 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **PONCELET, Olivier, Jean, Christian** [FR/FR]; Kodak Industrie, Département Brevets, CRT - Zone Industrielle, F-71102 Chalon sur Saône Cedex (FR). **DESROUSSEAU, Stéphanie, Véronique** [FR/FR]; KODAK INDUSTRIE, Département Brevets, CRT- Zone Industrielle, F-71102 Chalon Sur Saône Cedex (FR).
- (74) Agent: **HONORE, Anne-Claire**; Kodak Industrie, Département Brevets, CRT - Zone Industrielle, F-71102 Chalon sur Saône Cedex (FR).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR PREPARING AN ALUMINOSILICATE POLYMER AND THE POLYMER RESULTING FROM THIS METHOD

(57) Abstract: The present invention relates to a method for preparing an aluminosilicate polymer and the polymer resulting from this method. Said method consists in treating an aluminum halide with an alkyl orthosilicate only having hydrolyzable functions with an aqueous alkali, in the presence of silanol groups, aluminum concentration being maintained at less than 0.3 mol/l, the Al/Si molar ratio being maintained between 1 and 3.6 and the alkali/Al molar ratio being maintained between 2.3 and 3; and then in stirring the resulting mixture at ambient temperature in the presence of silanol groups for long enough to form the aluminosilicate polymer.

WO 2004/039724 A1

A METHOD FOR PREPARING AN ALUMINOSILICATE POLYMER
AND THE POLYMER RESULTING FROM THIS METHOD

FIELD OF THE INVENTION

The present invention relates to a method for preparing an
5 aluminosilicate polymer and to the polymer resulting from this method.

DESCRIPTION RELATIVE TO THE PRIOR ART

Aluminosilicate polymers are known in various forms. For example
aluminosilicate polymers are known in fiber form, such as imogolite. Imogolite is
a filamentary, tubular and crystallized aluminosilicate, present in the impure
10 natural state in volcanic ashes and certain soils; it was described for the first time
by Wada in J. Soil Sci. 1979, 30(2), 347-355. Imogolite can be synthesized with
various degrees of purity using different methods. A method for obtaining an
imogolite gel with a high degree of purity is described in Patent Application EP-A-
1 112 959. This method consists in treating a mixed aluminum and silicon
15 alkoxide with an aqueous alkali with pH between 4 and 6.5, by maintaining the
aluminum molar concentration between $5 \cdot 10^{-4}$ and 10^{-2} M and the Al/Si molar
ratio between 1 and 3, then heating the resulting mixture in the presence of silanol
groups for long enough to form the fibrous aluminosilicate polymer and eliminate
the residual ions from the reaction medium.

20 Aluminosilicate polymers are also known in spherical particle form.
Patent US-A-6,254,845 describes a method for preparing hollow spheres of
amorphous aluminosilicate polymer. This method consists in mixing at high speed
a silicon-based compound (0.01-1 mol/l) with an aluminum compound (0.01-1
mol/l) to form a suspension comprising a salt in solution as byproduct and
25 precursor particles, eliminating a portion of the salt in solution and subjecting the
precursor particles to heat treatment so as to obtain a porous material in the form
of aluminosilicate hollow spheres. This porous material can be used in deodorants,
humidity absorbers or in microencapsulated medicines.

SUMMARY OF THE INVENTION

The present invention provides a new method for preparing an aluminosilicate polymer and a new aluminosilicate polymer obtainable by this method.

5 The method of the present invention for preparing an aluminosilicate polymer, comprises the following steps:

- a) treating a mixed aluminum and silicon alkoxide only comprising hydrolyzable functions, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon compounds only comprising hydrolyzable functions, with an aqueous alkali, in the presence of silanol groups, the aluminum concentration being maintained at less than 0.3 mol/l, the Al/Si molar ratio being maintained between 1 and 3.6 and the alkali/Al molar ratio being maintained between 2.3 and 3;
- 10 b) stirring the mixture resulting from step (a) at ambient temperature in the presence of silanol groups long enough to form the aluminosilicate polymer; and
- c) eliminating the byproducts formed during steps a) and b) from the reaction medium.

20 Throughout the present description, the expression "hydrolyzable function" means a substituent eliminated by hydrolysis during the process and in particular at the time of treatment with the aqueous alkali. In the following, the expression "unmodified mixed aluminum and silicon alkoxide" or "unmodified mixed aluminum and silicon precursor" means respectively a mixed aluminum and silicon alkoxide only having hydrolyzable functions, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon compounds only having hydrolyzable functions. More generally, an "unmodified" compound is a compound that only comprises hydrolyzable substituents.

30 Step c) can be carried out according to different well-known methods, such as washing or diafiltration.

The present invention also relates to the aluminosilicate polymer material obtainable by the method defined above. This new polymer has an amorphous structure shown by electron diffraction. This material is characterized in that its Raman spectrum comprises in spectral region 200-600 cm^{-1} a wide band at $250 \pm 6 \text{ cm}^{-1}$, a wide intense band at $359 \pm 6 \text{ cm}^{-1}$, a shoulder at $407 \pm 7 \text{ cm}^{-1}$, and a wide band at $501 \pm 6 \text{ cm}^{-1}$, the Raman spectrum being produced for the material resulting from step b) and before step c).

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 represent the spectra obtained by Raman spectroscopy of comparative aluminosilicate polymers prepared according to the methods described in Patent Application EP-A-1,112,959 and in Patent US-A-6,254,845 respectively,

Figure 3 represents diagrammatically a device for carrying out steps a) and b) of the method according to the invention,

Figures 4 to 12 represent the spectra obtained by Raman spectroscopy of aluminosilicate polymers according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

According to one embodiment of the method according to the present invention, the unmodified mixed aluminum and silicon precursor is formed in situ by mixing in aqueous medium (i) one compound selected from the group consisting of aluminum salts, aluminum alkoxides and aluminum halogenoalkoxides and (ii) at least one compound selected from the group consisting of unmodified silicon alkoxides and chloroalkoxides. The alkoxide radical of the unmodified aluminum compound or silicon compound preferably contains 1 to 5 carbon atoms, such as methoxide, ethoxide, n-propoxide, or i-propoxide.

Preferably, an aluminum salt, such as a halide (e.g. chloride or bromide), a perhalogenate, a sulfate, a nitrate, a phosphate or a carboxylate, and at least one unmodified silicon alkoxide, such as tetramethyl or tetraethyl orthosilicate, is used.

A single unmodified silicon alkoxide or a mixture of unmodified silicon alkoxides, or a single unmodified silicon chloroalkoxide or a mixture of unmodified silicon chloroalkoxides, or a mixture of unmodified silicon alkoxides and chloroalkoxides can be used.

5 Preferably, an aluminum halide, such as chloride, and an unmodified silicon alkoxide is used. In practice, the mixture is made at ambient temperature between 15°C and 35°C, preferably between 20°C and 25°C, by adding the silicon alkoxide, pure or diluted in a co-solvent such as an alcohol, to the aluminum salt in aqueous solution, with stirring, until a clear homogeneous
10 mixture is obtained. An unmodified mixed aluminum and silicon precursor is thus obtained. The stirring time varies from 10 to 180 minutes, and is preferably 120 minutes.

 According to step a) of the method according to the invention, the precursor or an unmodified mixed aluminum and silicon alkoxide is put in contact
15 with an aqueous alkali, the aluminum concentration being maintained at less than 0.3 mol/l, the Al/Si molar ratio being maintained between 1 and 3.6, and the alkali/Al molar ratio being maintained between 2.3 and 3. Advantageously, the aluminum concentration is between 1.5×10^{-2} and 0.3 mol/l and even more preferably between 4.4×10^{-2} and 0.3 mol/l. Preferably, the Al/Si molar ratio is
20 between 1 and 2.

 Preferably, an aqueous solution of sodium, potassium or lithium hydroxide, diethylamine or triethylamine with concentration between 0.5 M and 3 M, and preferably 3 M is used. The alkali can also be in the form of an hydroalcoholic solution.

25 The alkali is added to the precursor or to the unmodified mixed aluminum and silicon alkoxide at a rate preferably between 50 and 650 mmol/hour.

 According to the invention, the addition of the alkali in step a) is performed in the presence of silanol groups. These groups can be supplied by glass
30 or silica (glass wool) particles or beads, which have superficial hydroxy groups. When the volume of liquid to be treated is large, it may be desirable to increase the

quantity of beads. The diameter of the beads can be between 0.2 mm and 5 mm and preferably between 1 mm and 3 mm. To simplify the implementation of the method according to the invention, the preparation of the mixed aluminum and silicon precursor can also be performed in the presence of silanol groups, for
5 example by circulating the mixture in a bed of glass beads.

After the addition of the alkali, step b) of the method according to the invention consists in stirring the mixture resulting from step a) at ambient temperature in the presence of silanol groups long enough to form the aluminosilicate polymer.

10 Then, step c) of the method according to the invention consists in eliminating from the reaction medium the byproducts formed during steps a) and b), such as the residual ions resulting essentially from the alkali used in step a). The residual ions can be eliminated by washing, by successive sedimentations or by diafiltration. The aluminosilicate polymer material according to the invention
15 resulting from step c) can then be concentrated by centrifugation or nanofiltration.

In a first embodiment of the method according to the invention, during step a) a quantity of alkali is added in order to obtain an alkali/Al molar ratio of about 2.3. In this case the pH is maintained between 4 and 5, and preferably between 4.2 and 4.3. Then step b) as described above is applied. The
20 aluminosilicate polymer material according to the present invention is thus obtained in dispersion form. Step c) to eliminate the residual ions can then be performed by diafiltration, followed by nanofiltration concentration.

In a second embodiment of the method according to the invention, during step a) a quantity of alkali is added to obtain an alkali/Al molar ratio of
25 about 3. Then step b) as described above is applied. The aluminosilicate polymer material according to the present invention is thus obtained in suspension form. Step c) to eliminate the residual ions can then be performed by diafiltration, followed by nanofiltration concentration, the aluminosilicate polymer material having been previously redispersed by adding acid, such as hydrochloric or acetic
30 acid or a mixture thereof.

In a third embodiment, the method according to the invention comprises an additional step d), after step b) and before step c). Said step d) consists in adding in a few minutes an additional quantity of aqueous alkali to reach an alkali/Al molar ratio of 3 if this ratio had not already been reached during step a). The aluminosilicate polymer material according to the present invention is thus obtained in suspension form. Step c) to eliminate the residual ions can then be performed by diafiltration, followed by nanofiltration concentration, the aluminosilicate polymer material having been previously redispersed by adding hydrochloric acid. Step c) can also be performed by washing with osmosed water by successive sedimentations, followed by centrifugation concentration.

The aluminosilicate polymer material according to the present invention resulting from step c) followed by concentration has physical gel form. The Al/Si molar ratio is between 1 and 3.6. Subsequent lyophilization enables the aluminosilicate polymer according to the invention to be obtained in solid form.

In another embodiment, the method according to the invention comprises an additional step e), after step c), by which at least one chelating agent of aluminum is added to the aluminosilicate polymer resulting from step c). Then the mixture is stirred. Subsequent evacuation by vacuum enables the aluminosilicate polymer according to the invention to be obtained in solid form.

Said chelating agent of aluminum can be selected from the group consisting of carboxylic acids, phosphonic acids, sulfonic acids, difunctional acids, their ester and anhydride components and amino acids. Preferably, the chelating agent of aluminum is selected from the group consisting of HCOOH , R_1COOH wherein R_1 is selected from the group consisting of $\text{CH}_3(\text{CH}_2)_n$, n being between 0 and 12, CF_3 , C_6H_5 , $(\text{C}_6\text{H}_5)_2$, substituted aromatic rings as in salicylic acid, $\text{C}_4\text{H}_4\text{S}$; $\text{R}_2\text{PO}(\text{OH})_2$ wherein R_2 is selected from the group consisting of CH_3 , C_6H_5 , $\text{R}_3\text{SO}_3\text{H}$ wherein R_3 is $\text{CH}_3(\text{CH}_2)_n$, n being between 0 and 5; $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, $n = 0-8$; aromatic difunctional acids as phthalic acid; $\text{HOOC}(\text{CH}_2)_n\text{PO}(\text{OH})_2$, $n = 2, 4$; hydroxy aliphatic acids; $\text{HOOC}(\text{CH}_2\text{OH})_n\text{COOH}$, $n = 1-2$; $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$. Preferably, the chelating agent is acetic acid.

The useful solvent of chelating agent of aluminum is generally water but another solvent miscible to water can be used in order to solubilize the chelating agent before its adding to the aluminosilicate polymer resulting from step c). Step e) can comprise a first adding of acetic acid and a following adding of another different chelating agent of aluminum. This method is particularly useful to help the chelation when the chelating agent comprises large bulky groups.

The amount of chelating agent of aluminum corresponds to a molar ratio between chelating functions of the chelating agent and aluminum of the aluminosilicate polymer, which can be greater than 0.1. Preferably, the molar ratio is comprised between 0.1 and 10, and preferably between 0.1 and 4.

The introduction of a chelating agent of aluminium allows to modify the surface of the aluminosilicate polymer by forming a chelate compound. The functional group of the chelating agent allows to increase the affinity of the aluminosilicate polymer with the medium in which it is used.

The Raman spectrum of the aluminosilicate polymer material resulting from step e) comprises the same bands as the aluminosilicate polymer material resulting from step b), as well as bands corresponding to the chelating agent in its chelate form.

The aluminosilicate polymer material according to the present invention resulting from step e) has physical gel form. The Al/Si molar ratio is between 1 and 3.6.

The following examples illustrate the present invention without however limiting the scope.

Example 1 (comparison)

Imogolite, fibrous aluminosilicate polymer, was prepared according to the method described in Patent Application EP-A-1,112,959.

364.5 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1.51 mole), then 127.7 g tetramethyl orthosilicate (0.84 mole) were added to 100 l of osmosed water. A transparent solution was obtained that was stirred for 30 minutes. The reaction mixture was circulated through a bed of glass beads 2 mm in diameter (Prolabo) using a pump with output 10 l/min. 3.46 l NaOH 1M were added in at least two hours. The

reaction medium became cloudy. It was stirred for three hours. The medium became clear. The pump was then disconnected. Then 1.063 l NaOH 1M were added. A white precipitate formed. This was left to settle overnight, and then the supernatant liquid was eliminated. About 30 liters of product remained. 0.6 l of a
5 50/50 by volume mixture of HCl, 1M and acetic acid, 2M was added to the precipitate. It was stirred for six hours. The mixture became clear and had a pH of 4.0. Then 146 liters of osmosed water were added. The final volume was 176 liters. The solution was ready for the maturation phase: the solution was left to stand in an inert plastic container (polypropylene) for ten days at ambient
10 temperature (about 20°C). Then, the mixture was heated to 96°C while stirring for 24 hours in a stainless steel reactor. Then the reaction medium was concentrated by ultrafiltration using an Amicon 100 K membrane. An imogolite type fibrous aluminosilicate polymer was obtained, shown by electron diffraction. The Raman spectrum of this polymer is represented by Figure 1.

15 In all the examples described, a Raman Bruker RFS 100 spectrometer (laser exciting wavelength, 1064 nm, power 800 mW, and 512 scans) was used to obtain the Raman spectra. The spectra were acquired in reflection mode (180°) using a lens with semi-cylindrical mirror. Samples were analyzed in solid form (obtained by lyophilization) without special preparation. Raman spectra
20 instead of infrared spectra were preferred, because the materials according to the invention were water rich and the infrared spectrum of the material was then masked by the water. This problem does not appear with Raman spectra technology. Materials that have the same Raman signature belong to the same family.

25 **Example 2 (comparison)**

An aluminosilicate polymer in hollow sphere form was prepared according to the method described in Patent US-A-6,254,845.

Sodium orthosilicate was dissolved in purified water to obtain 50 ml of an aqueous solution at 0.1 mol /l. Separately, aluminum chloride was
30 dissolved in purified water to obtain 67.15 ml of an aqueous solution at 0.1 mol /l. The aluminum chloride solution was mixed at high speed with the aqueous

solution of sodium orthosilicate. At this stage, the aluminum concentration was 5.7×10^{-2} mol/l. The Al/Si molar ratio was 1.34. The mixture was stirred for one hour at ambient temperature. A suspension was obtained that was filtered using a membrane filter to eliminate byproducts such as sodium chloride. The retentate
5 that adhered to the filter was recovered, and 120 ml of purified water was added to it. The mixture was dispersed using ultrasound for one hour and then warmed for five days at 80°C, washed with purified water, and dried in normal conditions of temperature and pressure. An aluminosilicate polymer was obtained in hollow spherical particle form. The Raman spectrum of this polymer is represented by
10 Figure 2.

Example 3 (invention)

With reference to Figure 3, 100 l of osmosed water were poured into a plastic (polypropylene) reactor (10). 4.53 moles $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, then 2.52 moles tetraethyl orthosilicate were added. This mixture was stirred and circulated
15 simultaneously through a bed formed of 1 kg of glass beads (11) 2-mm diameter using a pump (12) with 8-l/min output. The operation to prepare the unmodified mixed aluminum and silicon precursor took 90 minutes. Then, according to step a) of the method according to the invention, 10.5 moles NaOH 3M were added to the contents of the reactor (10) in two hours. Aluminum concentration was 4.4×10^{-2}
20 mol/l, Al/Si molar ratio 1.8 and alkali/Al ratio 2.31. The reaction medium clouded. According to step b) of the method according to the invention, the mixture was stirred for 48 hours. The medium became clear. The circulation was stopped in the glass bead bed. The aluminosilicate polymer material according to the present invention was thus obtained in dispersion form. Figure 4 represents the Raman
25 spectrum of this polymer that was lyophilized to obtain its Raman signature. Step c) of the method according to the invention consisted in performing pre-concentration by a factor of 3 by nanofiltration, then diafiltration using a Filmtec NF 2540 nanofiltration membrane (surface area 6 m²) to eliminate the sodium salts to obtain an Al/Na ratio greater than 100. The retentate resulting from the
30 diafiltration by nanofiltration was concentrated to obtain a gel with about 20% by weight of aluminosilicate polymer according to the invention.

Example 3 was repeated replacing tetraethyl orthosilicate by tetramethyl orthosilicate. The same Raman spectrum was obtained as that of Figure 4.

Example 4 (invention)

20 moles AlCl_3 , $6\text{H}_2\text{O}$, then 4.5 kg glass beads 2-mm diameter, then
5 11.1 moles tetraethyl orthosilicate were added to 100 l osmosed water. This mixture was stirred vigorously. The operation to prepare the unmodified mixed aluminum and silicon precursor took 30 minutes to obtain a clear homogeneous medium. Then, according to step a) of the method according to the invention, 60 moles NaOH dissolved in 100 liters of osmosed water were added to the reaction
10 medium in 30 minutes. The reaction medium clouded. Aluminum concentration was 0.1 mol/l, Al/Si molar ratio 1.8 and alkali/Al ratio 3. According to step b) of the method according to the invention, the mixture was stirred for 15 minutes. The aluminosilicate polymer material according to the present invention was thus obtained in suspension form. Figure 5 represents the Raman spectrum of this
15 polymer that was lyophilized to obtain its Raman signature. Step c) of the method according to the invention consisted in adding 930 g HCl 37% previously diluted 10 times and stirring for 150 minutes to obtain a dispersion of the aluminosilicate polymer according to the invention. The dispersion was then diafiltrated using a Filmtec NF 2540 nanofiltration membrane (surface area 6 m^2) to eliminate the
20 sodium salts to obtain an Al/Na ratio greater than 100. The retentate resulting from the diafiltration by nanofiltration was concentrated to obtain a gel with about 20% by weight of aluminosilicate polymer according to the invention.

Example 5 (invention)

4.53 moles AlCl_3 , $6\text{H}_2\text{O}$, then 2.52 moles tetraethyl orthosilicate
25 were added to 100 l osmosed water. This mixture was stirred and circulated simultaneously through a bed formed of 1-kg glass beads 2-mm diameter using a pump with 8-l/min output. The operation to prepare the unmodified mixed aluminum and silicon precursor took 120 minutes. Then, according to step a) of the method according to the invention, 10.5 moles NaOH 3M were added to the
30 precursor in two hours. The reaction medium clouded. According to step b) of the method according to the invention, the mixture was stirred for 15-20 hours. The

medium became clear. The circulation was stopped in the glass bead bed. Then, according to step d) of the method according to the invention, 3.09 moles NaOH 3M were added in ten minutes. Aluminum concentration was 4.4×10^{-2} mol/l, Al/Si molar ratio 1.8 and alkali/Al ratio 3. The aluminosilicate polymer material according to the present invention was thus obtained in suspension form. Figure 6 represents the Raman spectrum of this polymer that was lyophilized to obtain its Raman signature. Step c) of the method according to the invention consisted in leaving the polymer suspension to settle for 24 hours, then in discarding the supernatant to recover the sediment. This sediment was washed with osmosed water by successive sedimentations to obtain a sodium level in the supernatant less than 10 ppm. Then the sediment was centrifuged to obtain a gel with about 4% by weight of aluminosilicate polymer according to the invention. The resulting gel was lyophilized (20 mT, -50°C) to obtain a solid of constant mass. The aluminosilicate polymer material according to the invention was thus obtained in powder form. The powder can be redispersed by adding water and acid, such as hydrochloric or acetic acid, and with mechanical stirring.

Example 6 (invention)

The procedure of example 5 was repeated, except that step c) of the method according to the invention consisted in leaving the resulting polymer suspension to settle for 24 hours, then in discarding the supernatant to recover the sediment. Then 166 g HCl 37%, previously diluted 10 times, were added to the sediment to obtain a dispersion of the aluminosilicate polymer according to the invention. The dispersion was then diafiltrated using a Filmtec NF 2540 nanofiltration membrane (surface area 6 m²) to eliminate the sodium salts to achieve an Al/Na ratio greater than 100. Then the retentate resulting from the diafiltration by nanofiltration was concentrated to obtain a gel with about 20% by weight of aluminosilicate polymer according to the invention. The resulting gel was lyophilized (20 mT, -50°C) to achieve a solid of constant mass. The aluminosilicate polymer material according to the invention was thus obtained in powder form. The powder can be redispersed by adding water and acid, such as hydrochloric or acetic acid, and with mechanical stirring.

Example 7 (invention)

1.56 moles AlCl_3 , $6\text{H}_2\text{O}$, then 0.84 moles tetramethyl orthosilicate were added to 100 l osmosed water. This mixture was stirred and circulated simultaneously through a bed formed of 1-kg glass beads 2-mm diameter using a pump with 8-l/min output. The operation to prepare the unmodified mixed aluminum and silicon precursor took 120 minutes. Then, according to step a) of the method according to the invention, 3.5 moles NaOH 1M were added to the precursor in two hours. The reaction medium clouded. According to step b) of the method according to the invention, the mixture was stirred for 15-20 hours. The medium became clear. The circulation was stopped in the glass bead bed. Then, according to step d) of the method according to the invention, 1.06 moles NaOH 1M were added in ten minutes. Aluminum concentration was 1.5×10^{-2} mol/l, Al/Si molar ratio 1.8 and alkali/Al ratio 2.9. The aluminosilicate polymer material according to the present invention was thus obtained in suspension form. Step c) of the method according to the invention consisted in leaving the polymer suspension to settle for 24 hours, then discarding the supernatant to recover the sediment. This sediment was washed with osmosed water by successive sedimentations to obtain a sodium level in the supernatant less than 10 ppm. Then the sediment was centrifuged to obtain a gel with about 4% by weight of aluminosilicate polymer according to the invention. The resulting gel was lyophilized (20 mT, -50°C) to achieve a solid of constant mass. The aluminosilicate polymer material according to the present invention was thus obtained in powder form. The powder redispersed by adding water and acid, such as hydrochloric or acetic acid, and with mechanical stirring.

Example 8 (invention)

31.3 moles AlCl_3 , $6\text{H}_2\text{O}$, then 16.79 moles tetraethyl orthosilicate were added to 100 l osmosed water. This mixture was stirred and circulated simultaneously through a bed formed of 1-kg glass beads 2-mm diameter using a pump with 8-l/min output. The operation to prepare the unmodified mixed aluminum and silicon precursor took 120 minutes. Then, according to step a) of the method according to the invention, 70 moles NaOH 20M were added to the

precursor in two hours. The reaction medium clouded. According to step b) of the method according to the invention, the mixture was stirred for 15-20 hours. The medium became clear. The circulation was stopped in the glass bead bed. Then, according to step d) of the method according to the invention, 21.5 moles NaOH
5 20M were added in ten minutes. Aluminum concentration was 0.3 mol/l, Al/Si molar ratio 1.9 and alkali/Al ratio 2.9. The aluminosilicate polymer material according to the present invention was thus obtained in suspension form. Step c) of the method according to the invention consisted in leaving the polymer suspension to settle for 24 hours, then in discarding the supernatant to recover the
10 sediment. This sediment was washed with osmosed water by successive sedimentations to obtain a sodium level in the supernatant less than 10 ppm. Then the sediment was centrifuged to obtain a gel with about 4% by weight of aluminosilicate polymer according to the invention. The resulting gel was lyophilized (20 mT, -50°C) to achieve a solid of constant mass. The
15 aluminosilicate polymer material according to the present invention was thus obtained in powder form. The powder can be redispersed by adding water and acid, such as hydrochloric or acetic acid, and with mechanical stirring.

Example 9 (invention)

100 g of gel of aluminosilicate polymer obtained in Example 6 (Al
20 amount = 1,54 g, 57 mmol, measured by inductively coupled plasma atomic emission spectroscopy, ICP) was diluted with 100 g of osmosed water. Glacial acetic acid (6.8 g, 114 mmol) was added to the gel. The mixture was stirred during 2 days. The excess of water and the unreacted acetic acid were removed by evacuation under vacuum at 35°C. 11.1 g of a white powder was obtained. The
25 Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 7. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands corresponding to the chelating agent in its acetate form.

Example 10 (invention)

30 Methyl phosphonic acid powder (1.7 g, 10.4 mmol) was solubilized in ethanol (10 ml). 40g of gel of aluminosilicate polymer (Al amount = 0.950 g, 35

mmol) obtained in Example 6 diluted with 20g of osmosed water were added to the alcoholic solution of methyl phosphonic acid. The mixture was stirred during 4 days. The excess of ethanol was removed by evacuation under vacuum at 35°C. A white powder was obtained. The Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 8. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands corresponding to the chelating agent in its phosphonate form.

Example 11 (invention)

20 g of gel of aluminosilicate polymer (Al amount = 0.8 g, 29 mmol) obtained in Example 6 was diluted with 20 g of osmosed water. Methyl sulfonic acid (1.6 g, 16.6 mmol) was added to the gel. The mixture was stirred during 4 days. The excess of water was removed by evacuation under vacuum at 35°C. A white powder was obtained. The Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 9. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands corresponding to the chelating agent in its sulfonate form.

Example 12 (invention)

Benzoic acid powder (0.85 g, 7 mmol) was solubilized in 40 ml of ethanol then 40 g of the aluminosilicate polymer gel (Al amount = 0.97 g, 36 mmol) obtained in Example 6 diluted in 20 ml osmosed water was added to the alcoholic solution. The mixture was stirred during 3 days. The excess of ethanol and water was removed under vacuum at 35°C. A white powder is obtained. The Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 10. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands corresponding to the chelating agent in its benzoate form.

Example 13 (invention)

Benzoic acid powder (0.3 g, 2.5 mmol) was solubilized in 10 ml of ethanol then 1g of the aluminosilicate polymer modified with acetic acid described in example 9 (Al amount = 0,13 g, 5.1 mmol) was added to the alcoholic solution.

- 5 The mixture was stirred during 3 days. The excess of ethanol was removed under vacuum at 35°C. A white powder is obtained. The Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 11. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands corresponding to the
10 chelating agent in its benzoate form and in its residual acetate form.

Example 14 (invention)

100 g of gel of aluminosilicate polymer obtained in Example 6 (Al amount = 1,54 g, 57 mmol) was diluted with 100 g of osmosed water. Propionic acid (2.0 g, 27.7 mmol) was added to the gel. The mixture was stirred during 2

- 15 days. The excess of water and the unreacted acetic acid were removed by evacuation under vacuum at 35°C. A white powder was obtained. The Raman spectrum of this aluminosilicate polymer material according to the invention is represented by Figure 12. The Raman spectrum comprises the bands of the aluminosilicate polymer obtained in Example 6, as well as the bands
20 corresponding to the chelating agent in its propionate form.

CLAIMS

1. A method for preparing an aluminosilicate polymer,
comprising the following steps:

- 5 a) treating a mixed aluminum and silicon alkoxide only comprising hydrolyzable functions, or a mixed aluminum and silicon precursor resulting from the hydrolysis of a mixture of aluminum compounds and silicon compounds only comprising hydrolyzable functions, with an aqueous alkali, in the presence of silanol groups, the aluminum concentration being maintained at less than 0.3 mol/l, the
- 10 Al/Si molar ratio being maintained between 1 and 3.6 and the alkali/Al molar ratio being maintained between 2.3 and 3;
- b) stirring the mixture resulting from step a) at ambient temperature in the presence of silanol groups long enough to form the aluminosilicate polymer; and
- 15 c) eliminating the byproducts formed during steps a) and b) from the reaction medium.

2. The method according to Claim 1, wherein the alkali of step a) is selected from among the group consisting of sodium, potassium, and lithium hydroxide, diethylamine and triethylamine.

20

3. The method according to Claim 1, wherein the silanol groups are supplied in silica or glass bead form.

25 4. The method according to Claim 3, wherein the silica or glass beads have a diameter between 0.2 mm and 5 mm.

5. The method according to Claim 1, wherein the aluminum concentration is maintained between 1.5×10^{-2} and 0.3 mol/l.

6. The method according to Claim 1, wherein the aluminum concentration is maintained between 4.4×10^{-2} and 0.3 mol/l.

7. The method according to Claim 1, wherein said alkali/Al
5 molar ratio is about 2.3.

8. The method according to Claim 1, wherein said alkali/Al molar ratio is about 3.

10 9. The method according to Claim 1, comprising, after step b) and before step c), a step d), by which alkali is added in order to reach an alkali/Al molar ratio of 3 if this ratio has not already been reached in step a).

10. The method according to Claim 1, wherein the mixed
15 aluminum and silicon precursor resulting from hydrolysis of a mixture of aluminum compounds and silicon compounds only having hydrolyzable functions is a product resulting from the mixture in an aqueous medium (i) of a compound selected from the group consisting of aluminum salts, aluminum alkoxides and aluminum halogenoalkoxides and (ii) at least one compound selected from the
20 group consisting of silicon alkoxides and chloroalkoxides only having hydrolyzable functions.

11. The method according to Claim 10, wherein the mixed aluminum and silicon precursor is the product resulting from the mixture (i) of an
25 aluminum halide and (ii) a silicon alkoxide only having hydrolyzable functions.

12. The method according to Claim 11, wherein said silicon alkoxide only having hydrolyzable functions is tetramethyl orthosilicate or tetraethyl orthosilicate.

13. The method according to Claim 1, comprising, after step c), a step e), by which at least one chelating agent of aluminum is added to the aluminosilicate polymer resulting from step c).

5 14. The method according to Claim 13, wherein said chelating agent of aluminum is selected from the group consisting of carboxylic acids, phosphonic acids, sulfonic acids, difunctional acids, their ester and anhydride components and amino acids.

10 15. The method according to Claim 14, wherein said chelating agent of aluminum is selected from the group consisting of HCOOH, $R_1\text{COOH}$ wherein R_1 is selected from the group consisting of $\text{CH}_3(\text{CH}_2)_n$, n being between to 0 and 12, CF_3 , C_6H_5 , $(\text{C}_6\text{H}_5)_2$, substituted aromatic rings, $\text{C}_4\text{H}_4\text{S}$; $\text{R}_2\text{PO}(\text{OH})_2$ wherein R_2 is selected from the group consisting of CH_3 , C_6H_5 ; $\text{R}_3\text{SO}_3\text{H}$ wherein
15 R_3 is $\text{CH}_3(\text{CH}_2)_n$, n being between to 0 and 5; $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, $n = 0-8$; aromatic difunctional acids; $\text{HOOC}(\text{CH}_2)_n\text{PO}(\text{OH})_2$, $n = 2, 4$; hydroxy aliphatic acids; $\text{HOOC}(\text{CH}_2\text{OH})_n\text{COOH}$, $n = 1-2$; $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$.

16. The method according to Claim 13, wherein step e)
20 comprises a first adding of acetic acid and a following adding of another different chelating agent of aluminum.

17. The method according to Claim 13, wherein the amount of chelating agent of aluminum corresponds to a molar ratio between chelating
25 functions of the chelating agent and aluminum of the aluminosilicate polymer comprised between 0.1 and 10.

18. A material obtainable by the method according to Claim 1.

30 19. The material according to Claim 18, characterized in that its Raman spectrum comprises in spectral region $200-600\text{ cm}^{-1}$ a wide band at 250 ± 6

cm^{-1} , a wide intense band at $359 \pm 6 \text{ cm}^{-1}$, a shoulder at $407 \pm 7 \text{ cm}^{-1}$, and a wide band at $501 \pm 6 \text{ cm}^{-1}$, the Raman spectrum being produced for the material resulting from step b) and before step c).

1/12

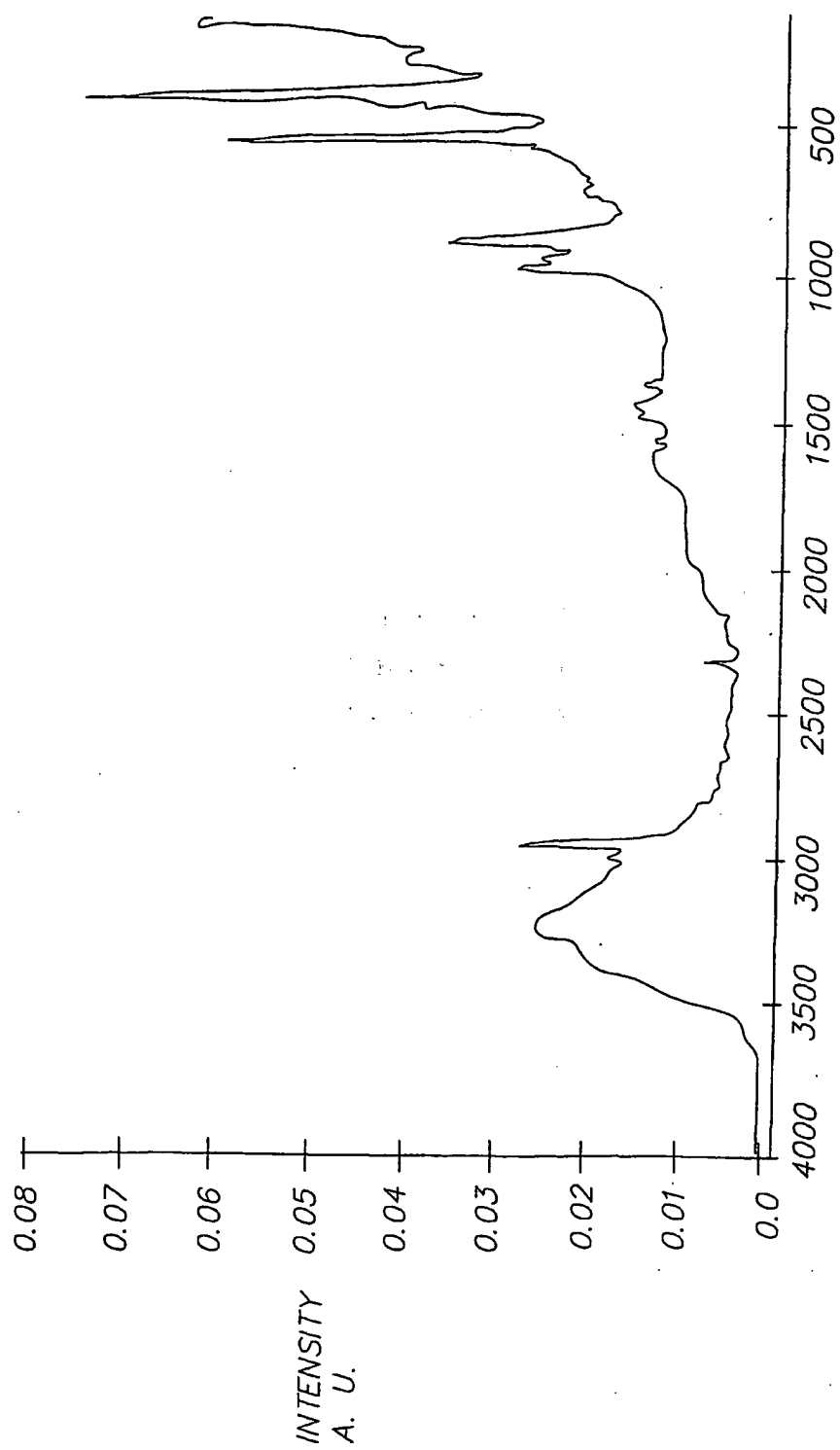
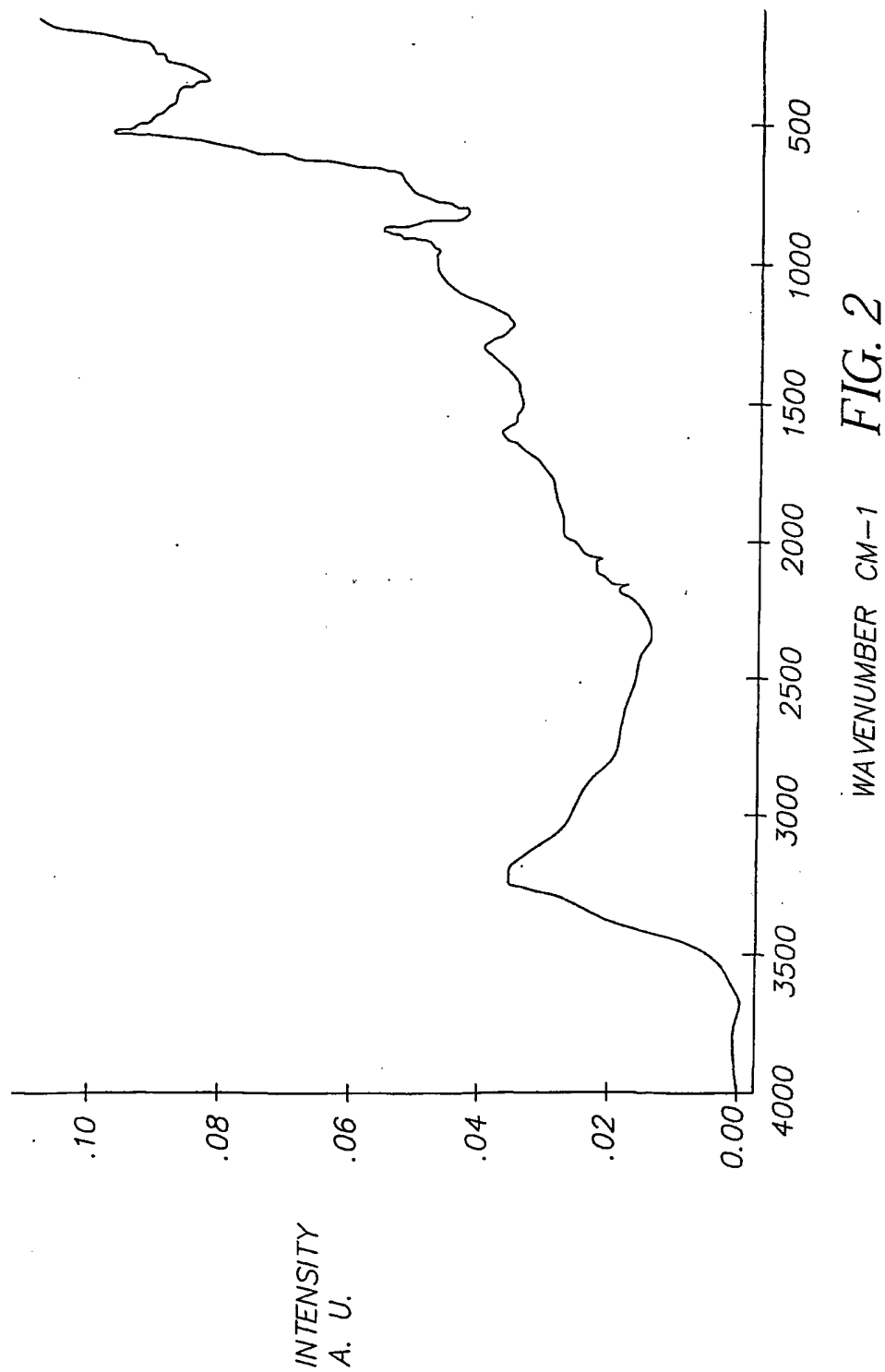


FIG. 1

2/12



3/12

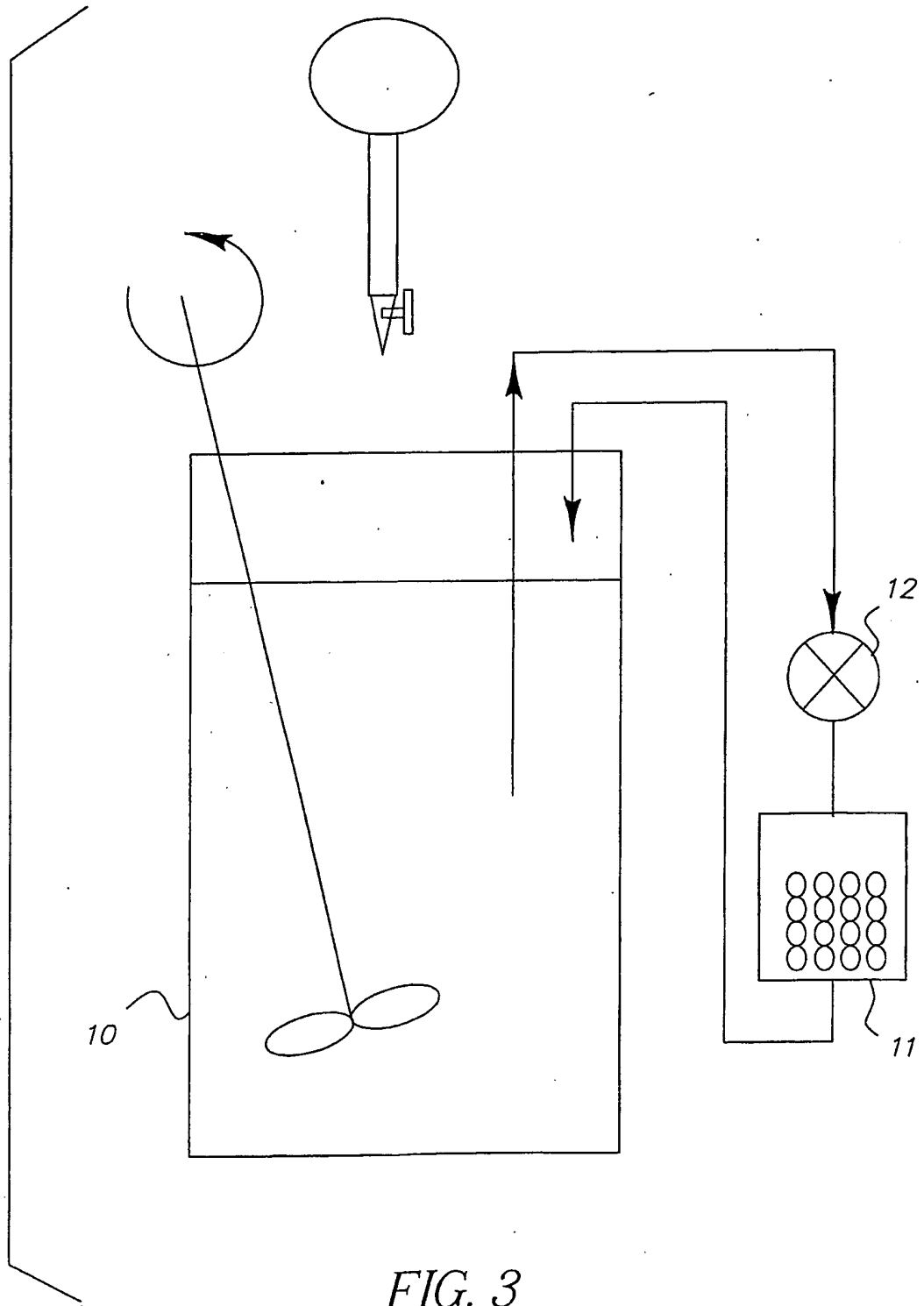
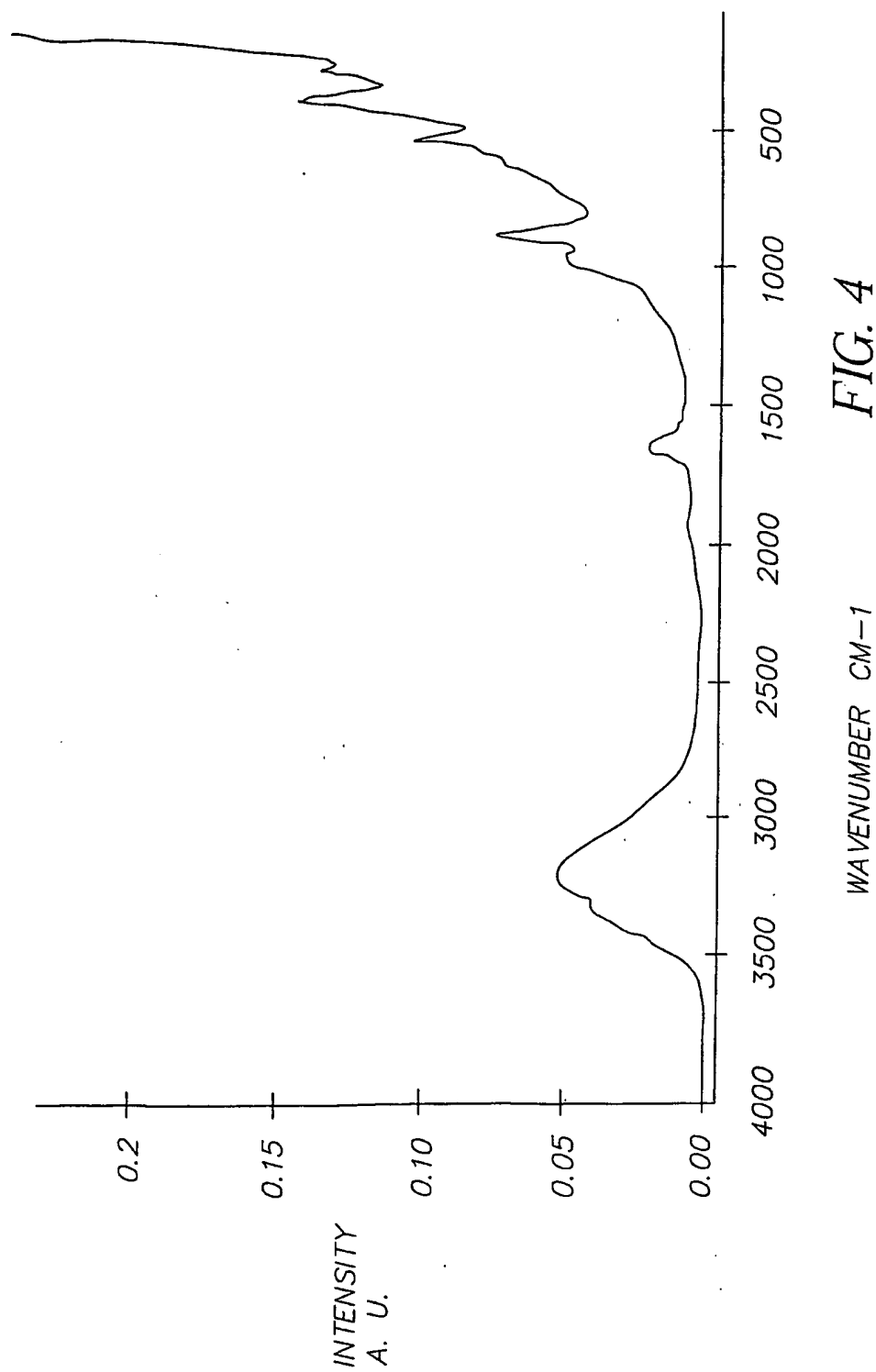


FIG. 3

4/12



5/12

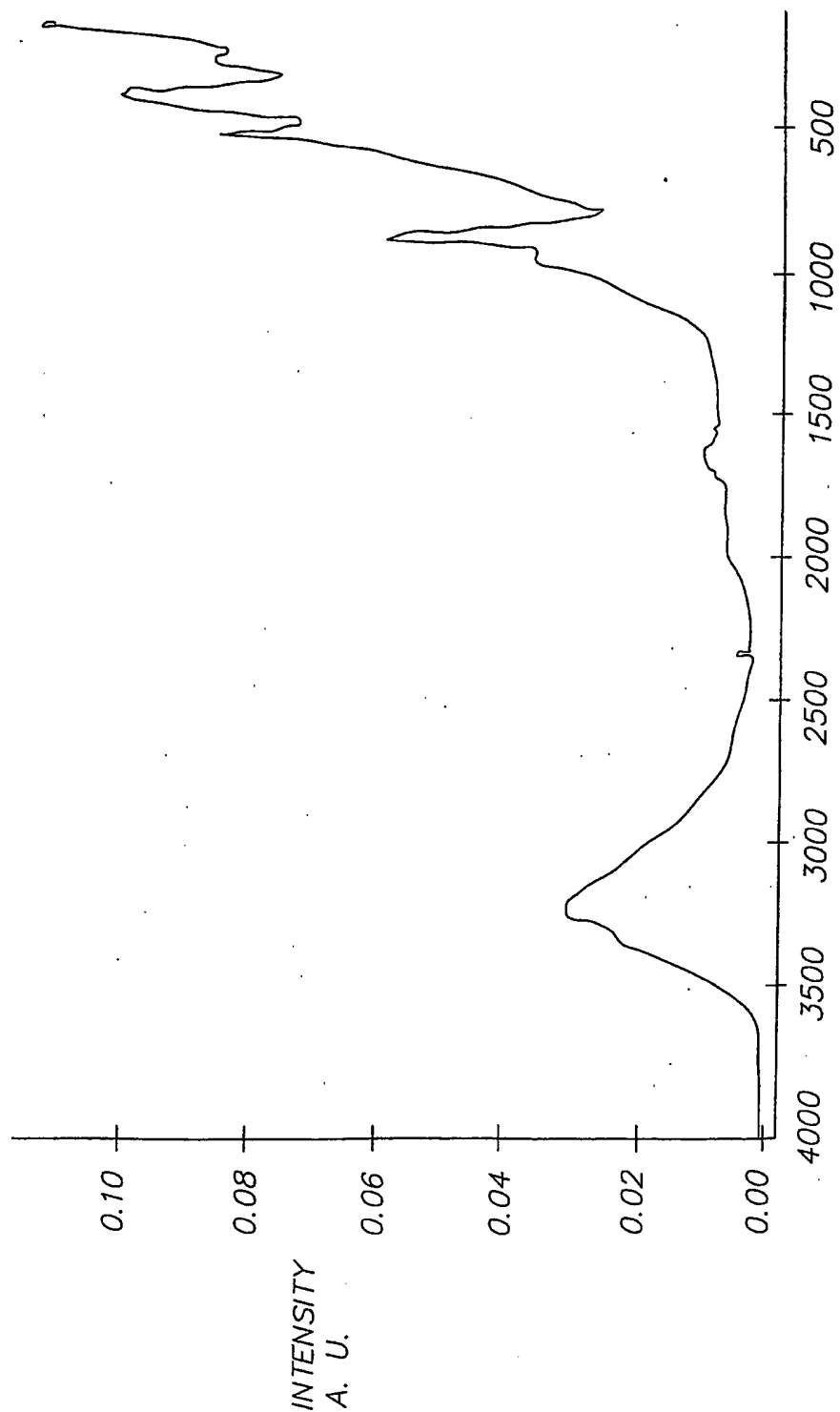


FIG. 5

6/12

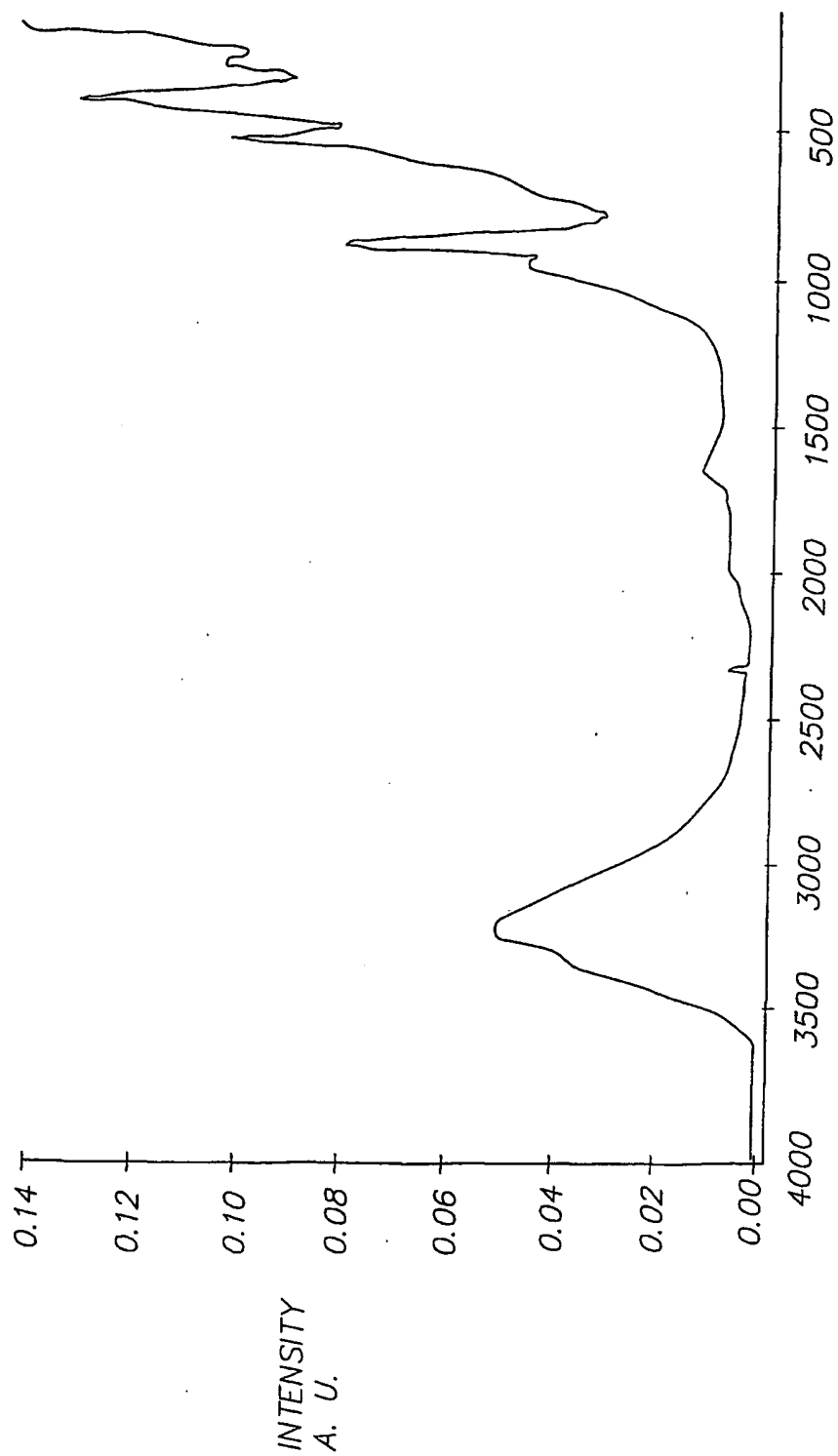


FIG. 6

WAVENUMBER CM-1

7/12

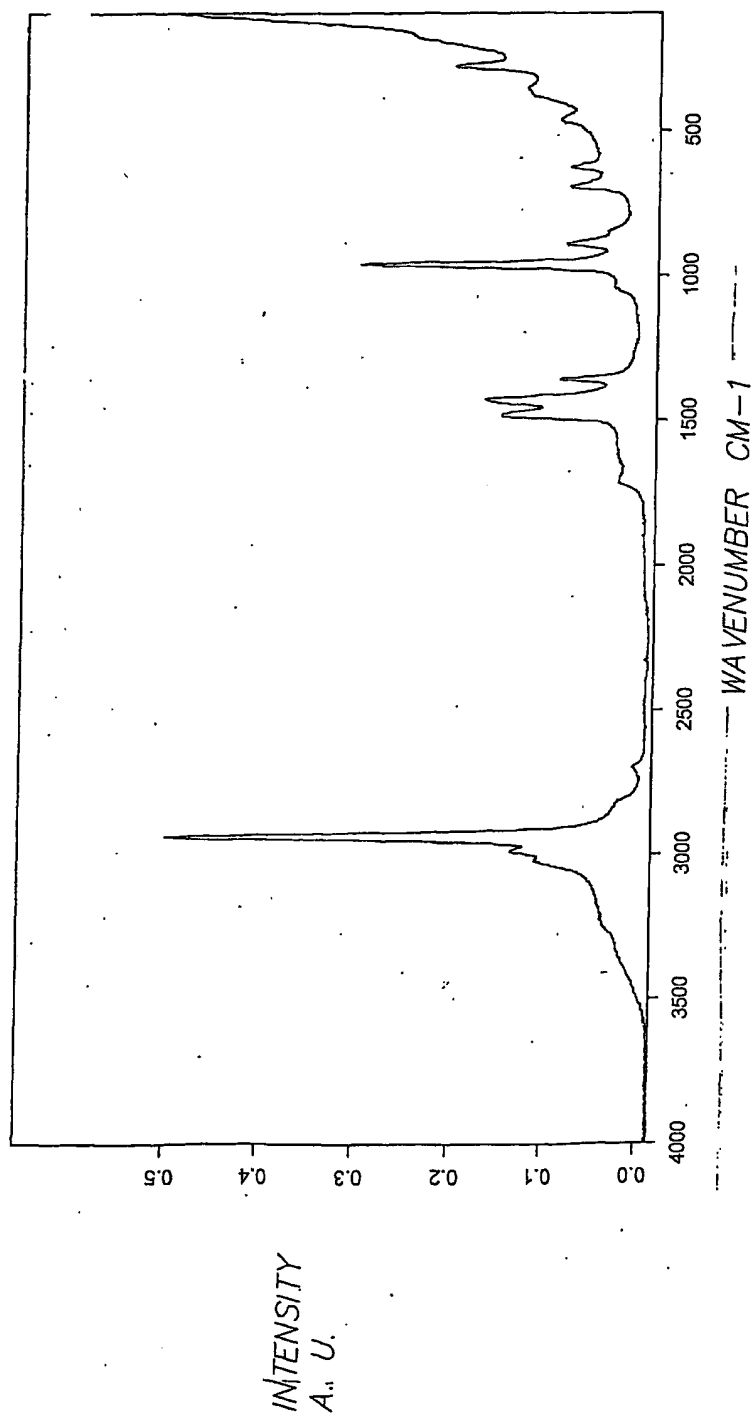


FIG. 7

8/12

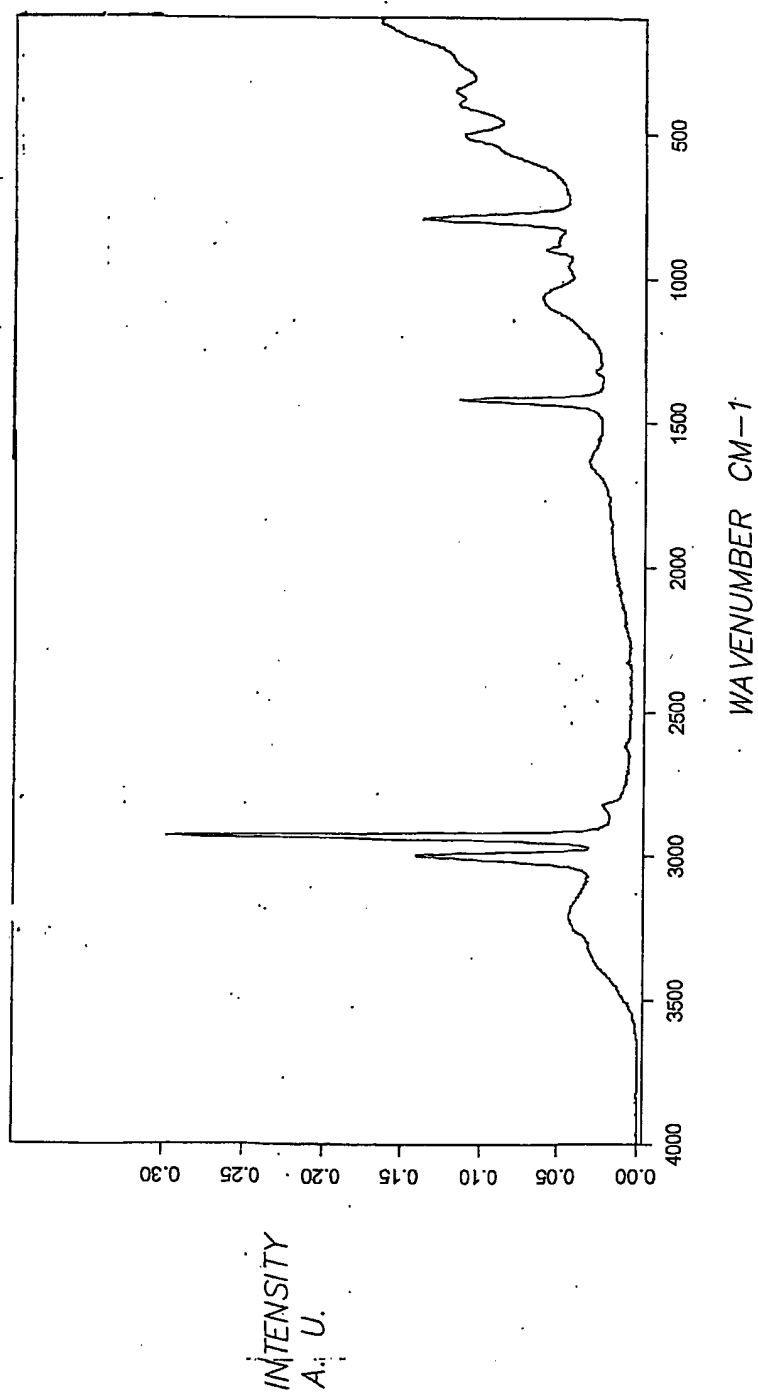


FIG. 8

9/12

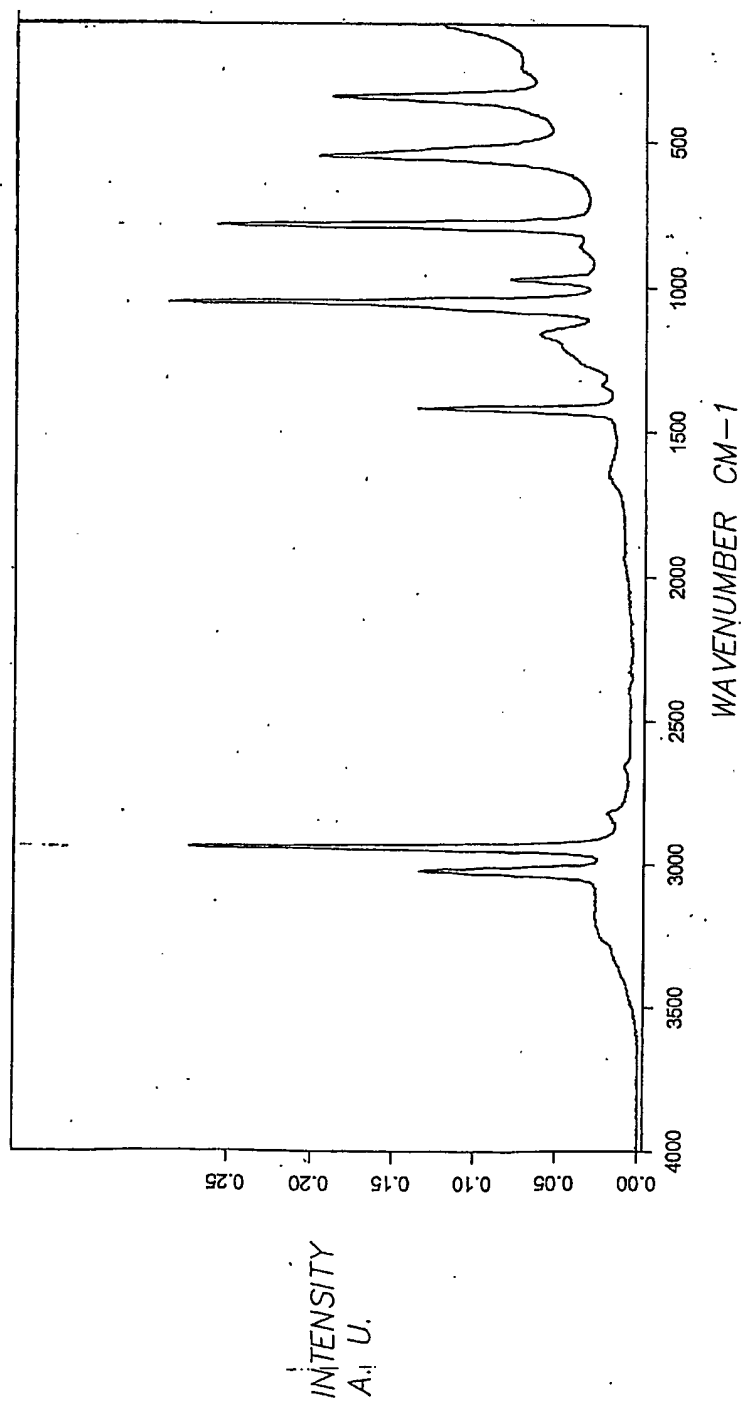


FIG. 9

10/12

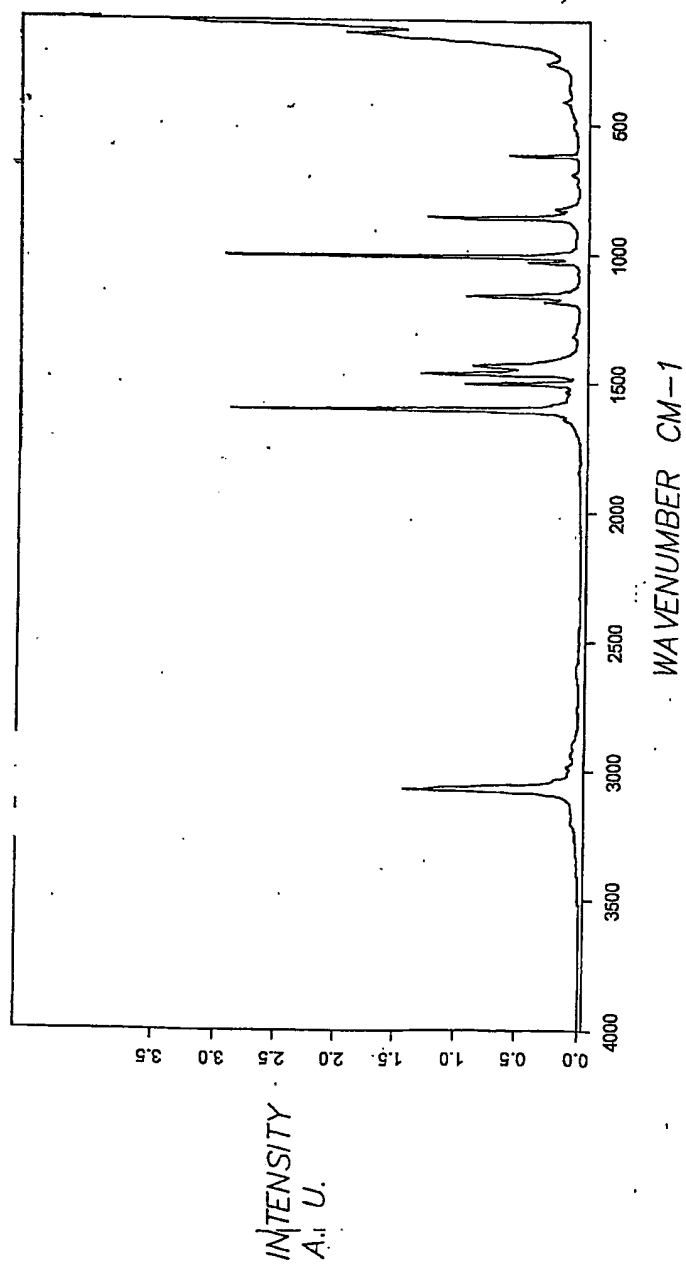


FIG. 10

11/12

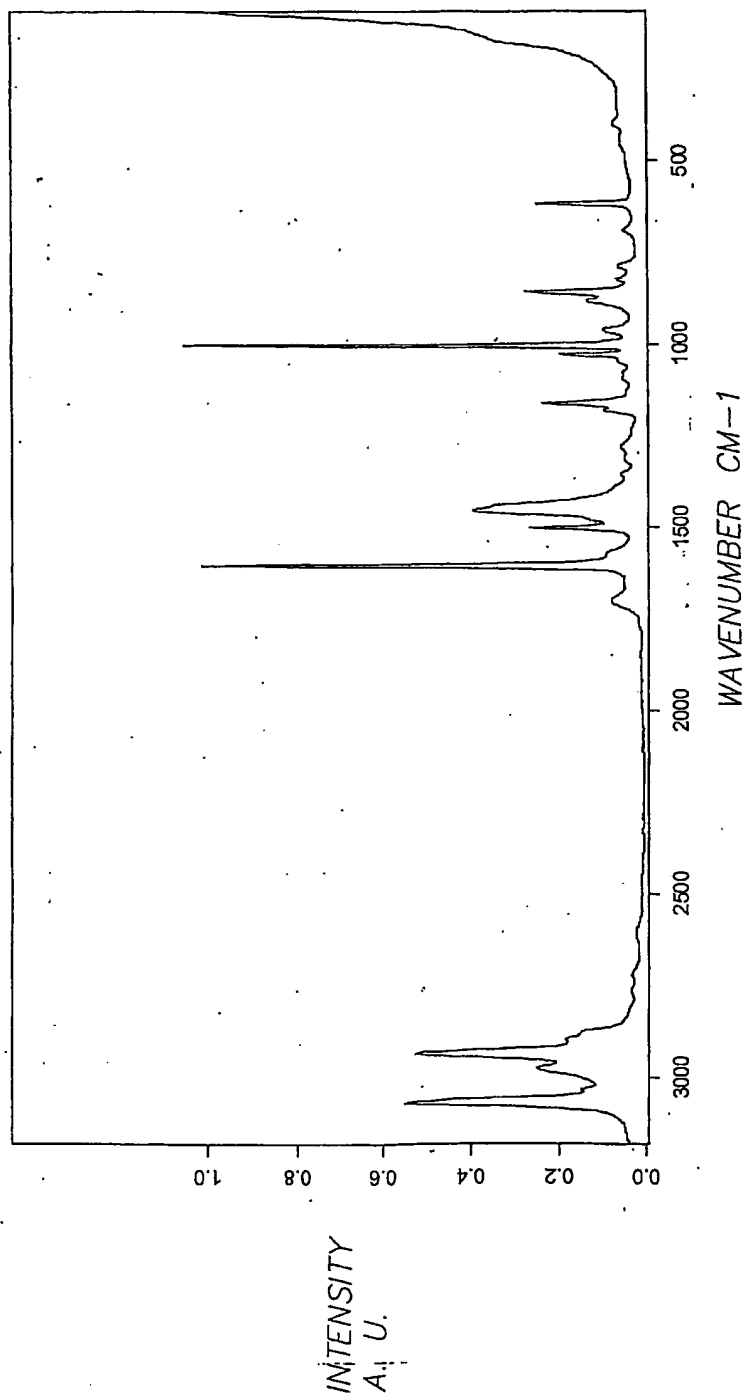
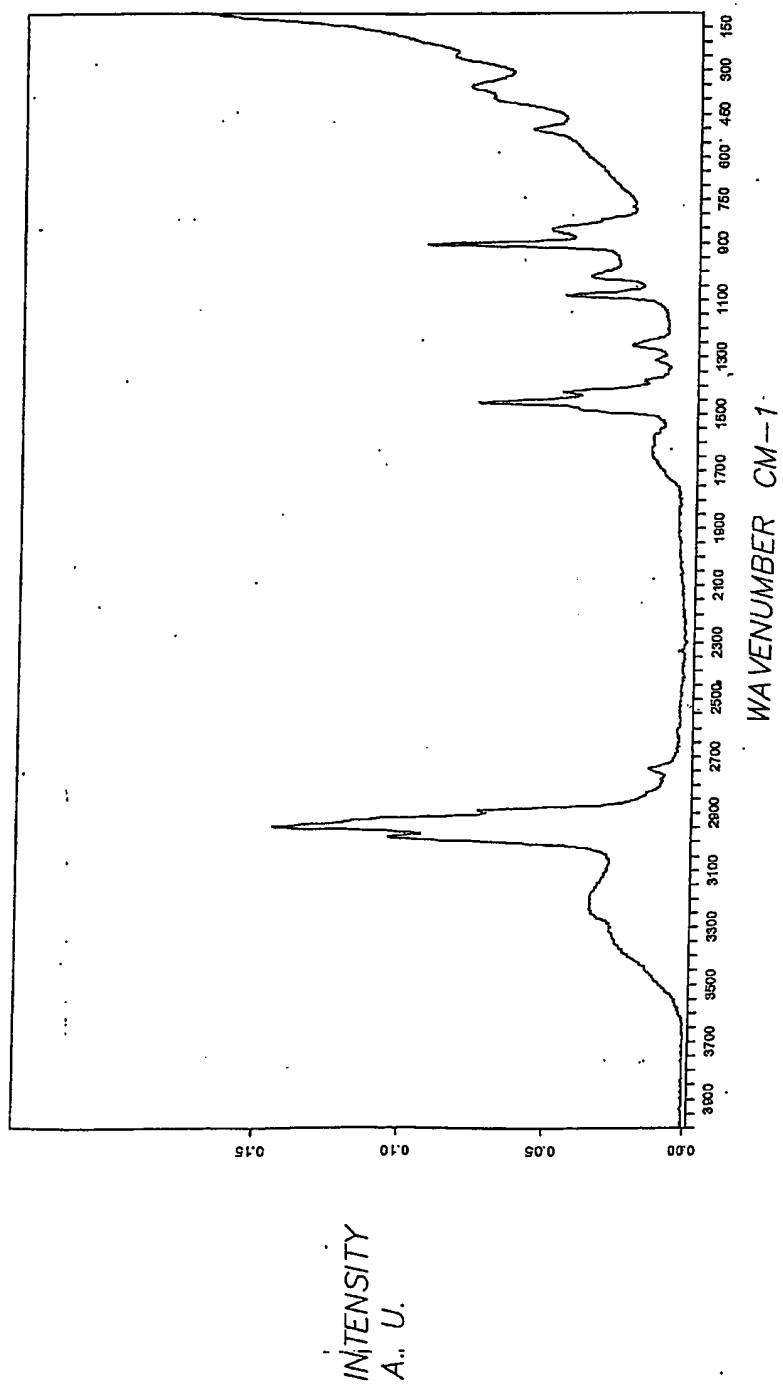


FIG. 11

12/12



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/07579

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B33/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 112 959 A (EASTMAN KODAK COMPANY) 4 July 2001 (2001-07-04) cited in the application the whole document	1-19
A	EP 0 895 965 A (EASTMAN KODAK COMPANY) 10 February 1999 (1999-02-10)	
A	WO 96 13459 A (EASTMAN KODAK COMPANY) 9 May 1996 (1996-05-09)	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

4 November 2003

Date of mailing of the international search report

14/11/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/07579

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1112959	A	04-07-2001	FR 2802912 A1	29-06-2001
			US 2002085972 A1	04-07-2002
			EP 1112959 A1	04-07-2001
			JP 2001226114 A	21-08-2001
EP 0895965	A	10-02-1999	FR 2767128 A1	12-02-1999
			DE 69801966 D1	15-11-2001
			DE 69801966 T2	16-05-2002
			EP 0895965 A1	10-02-1999
			JP 11130421 A	18-05-1999
			US 6296825 B1	02-10-2001
			US 2001046467 A1	29-11-2001
WO 9613459	A	09-05-1996	DE 69518909 D1	26-10-2000
			DE 69518909 T2	05-04-2001
			WO 9613459 A1	09-05-1996
			EP 0741668 A1	13-11-1996
			JP 9507826 T	12-08-1997
			US 5888711 A	30-03-1999